Janus particles with coupled electric and magnetic moments make a disordered magneto-electric medium

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We demonstrate that by combining permanent electric and magnetic moments in particles, it is possible to realize a new type of medium that allows for a cross-correlation between electric and magnetic properties of matter, known as magnetoelectric coupling. Magnetoelectric materials have so far been restricted to systems that exhibit long-range order in their electric and magnetic moments. Here, we show that a room-temperature, switchable magnetoelectric can be realized that is naturally disordered. The building blocks are Tellegen particles that orient in either an electric or a magnetic field.

PACS numbers: 75.80.+q,75.50.Tt,77.84.Lf

For a static electric field to give rise to a magnetization and similarly for a static magnetic field to induce an electric polarization in matter requires materials that exhibit special symmetries. Known magnetoelectric materials are single-phase non-centrosymmetric magnetic crystals or composites that contain a piezoelectric phase [1, 2, 3]. Most materials, however, are naturally disordered and so it is important to establish whether a disordered medium can support magnetoelectric (ME) phenomena. Conceivably the most general, random system is a gas or a liquid. If it consists of electric dipolar molecules, then application of an electric field would exert a torque and align the molecules with the field. Should the molecules also possess a magnetic moment parallel to the axis of the electric dipole moment, then orienting one moment should fix the other in space, provided the electric and magnetic dipoles are 'tied together'. However, van Vleck showed that this simple idea cannot be realized with molecules, such as nitric oxide (NO), even though NO is electric dipolar and has a magnetic moment [4]. The reason is that the magnetic moment in paramagnetic molecules is not of fixed orientation in the absence of a magnetic field [4, 5]. It follows that no magnetization can be induced in such an isotropic molecular medium, when only an electric field is applied.

The idea of coupled electric and magnetic dipole moments that preferentially align with a field may, however, still be realized, if the ME building-block is an electric-dipolar ferromagnetic particle as seen in Figure 1a. Once magnetized, each particle carries its own magnetic field which renders it anti-symmetric under time reversal symmetry and thus allows for ME effects [5]. An isotropic medium made of particles that have coupled permanent electric and magnetic moments (see Figure 1b) has first been considered by Tellegen, when he conceived of a fifth circuit element of an electrical network, the "gyrator" [6, 7]. Remarkably, Tellegen's proposal to make orientable microscopic magnets coupled to electrets has never been realized before [1, 8]. A few experimental studies consider Tellegen's proposal, but none of these are based on particles with permanent coupled electric and magnetic dipole moments [9, 10, 11]. Here we show

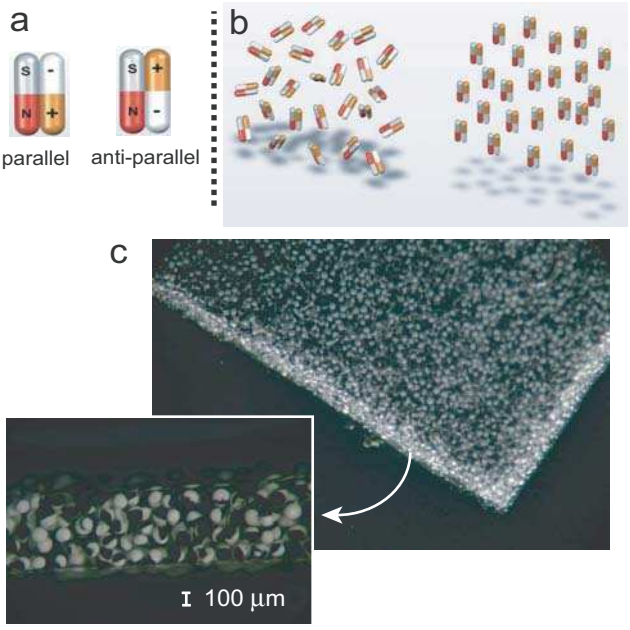

FIG. 1: (color online) Magnetoelectic particles: (a) Schematic of a magnetoelectric particle with electric and dipole moments parallel (left) and anti-parallel (right) [12]. (b) Magetoelectric medium with anti-parallel moments in a disordered state (left) and when it is ordered by application of either an external electric or a magnetic field (right). (c) Image of an elastomer sheet containing ME bichromal particles. The inset shows a magnified cross section of the sheet.

that magnetoelectric particles can be made and, moreover, that they can be dispersed randomly in a matrix to make a disordered material that exhibits a sizeable ME response. In this new class of materials the ME effect is based on the dynamics of the microscopic particles.

There are many examples of micro- and nanoparticles that are either electric or magnetic dipolar. For the present study it is required that both moments are present and that they are 'tied together'. Further, it is convenient if these particles are also optically anisotropic, as this can serve as an independent measure of the par-

ticles' alignment with an applied field [13, 14] and hence their ME response. Two-faced, "Janus" particles [15] that are separately electrically dipolar [13, 16, 17, 18] or ferromagnetic [14, 19] have been made. It should thus be possible to combine these characteristics. This is indeed the case, and we have for instance used fluorescent silica particles to make magnetoelectric Janus particles [5]. However, our aim here is not only to make magnetoelectric particles, but to also obtain and measure appreciable induced bulk magnetizations and electric polarizations. This requires large number densities and it becomes necessary to disperse the particles such that they do not interact too strongly with each other, since large dipole moments in close proximity favor an anti-parallel coupling and would thus preclude orientation by an external field. It is therefore advantageous to disperse the magnetoelectric particles in a suitable medium that acts as a spacer and prevents agglomeration of the particles, while still allowing for their rotation. For these reasons the magnetoelectric medium of this Letter is based on a system used for electronic paper (Gyricon) [20].

The system consists of spherical 100 μm polyethylene particles which are isotropically dispersed in a sheet of elastomer such that each particle occupies a small fluid cavity in which it is free to rotate [16, 20]. Each bead-like particle is electrically dipolar as the two differently-colored hemispheres have opposite electric charges. Here we show that these beads can also be made to carry a permanent magnetic moment, if made with a ferromagnetic pigment/powder [5]. The strength of the magnetic moment can be adjusted by varying the amount and nature of the ferromagnetic dopant. Once dispersed

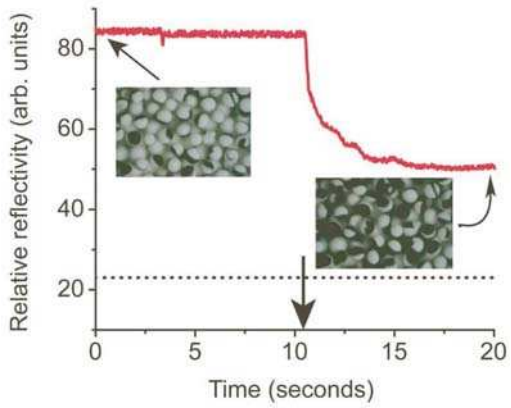

FIG. 2: (color online) Typical randomization of the elastomer sheet containing magnetoelectric beads. A voltage is applied and the beads are first predominately white-side up (image on the left). After the electric field is switched off (vertical marker), the beads quickly reorient to form a disordered medium (image on the right). The speed and dynamics of the reorientation depends on the size of the fluid cavity and the strength of the applied electric field. The dotted line indicates the reflectivity for black-side up. Similar switching can be observed visually when a magnetic field is applied.

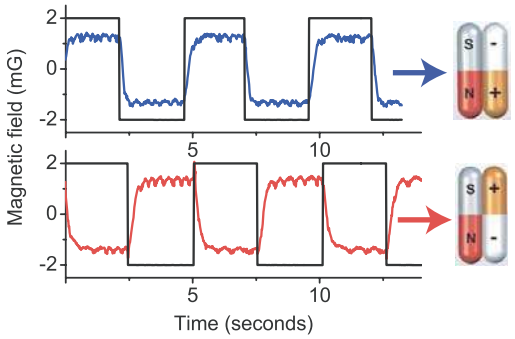

FIG. 3: (color online) Measured magnetic field as an electric field (voltage) is applied across the ME material. A 0.2 Hz square wave of 350 volts (black line, no scale indicated) is applied to the sheets of Fig. 1. In one sheet the particles' electric and magnetic moments are parallel (top) and in the other they are anti-parallel (bottom). The electric field induces a magnetization which give rises to a magnetic field (where 1mG = 10^{-7} T) that is in phase (parallel, blue trace) and out of phase (antiparallel, red trace) with the applied electric field.

in the elastomer, the beads are oriented by an electric field and magnetized, such that the permanent electric and magnetic moments of each bead are either parallel, or anti-parallel. The sheet now contains randomly dispersed magnetoelectric particles (Fig. 1c).

Because the axis of the optical anisotropy of the beads is also the axis of their electric and magnetic moments, the measured intensity of reflected light can serve as an optical measure of the average orientation of the beads and thus the total ME response. In the present ME system, the particle interactions are weak enough to permit orientation by the field, but strong enough to cause the beads to randomize in the absence of the field. In Figure 2 it is seen that once the aligning field has been switched off, the sheet turns from white to gray as the beads become randomly oriented. In the absence of any field the medium may thus be characterized as being disordered and isotropic, yet containing particles that exhibit magnetoelectric coupling. This is in contrast to all known magnetoelectric media that even in the absence of any fields contain at least one phase that is ordered [1, 2, 3, 21]. In addition to optical measurements, we are able to directly record the ME response of the medium (further information is available online [5]). The sheet is contained between two conductive transparent windows that make a capacitor and a voltage may be applied across the capacitor such that the oriented particles give rise to a magnetic field. This is detected with a fluxgate magnetometer. The functional form of the detected magnetic field closely follows the applied electric field (voltage), as can be seen in Figure 3. Similarly, upon application of a magnetic field provided by a solenoid, a voltage is recorded on an electrometer. The electrical detection is more challenging, and it is seen that the detected voltage does not exactly follow the applied magnetic field, as

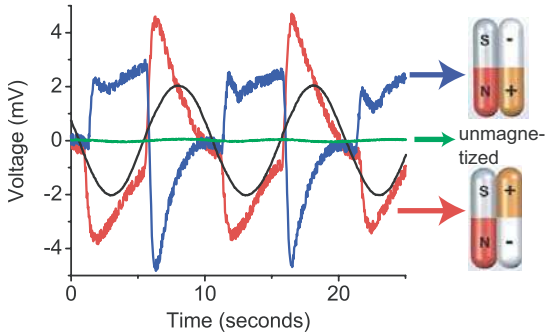

FIG. 4: (color online) Voltage resulting from application of a sinusoidal magnetic field with an amplitude of 90 Gauss at 0.1 Hz (black line, no scale indicated). The unmagnetized sheet does not give rise to a voltage (green trace). The same sheet is now magnetized such that the electric and magnetic moments of the ME particles are parallel (blue trace), and then re-magnetizationed such that the moments are anti-parallel (red trace). The slow driving field ensures that pick-up is minimal, but at these frequencies an asymmetry in the bead rotation can be observed, which is explained by the presence of shallowly trapped charges in the adhesion layer [5].

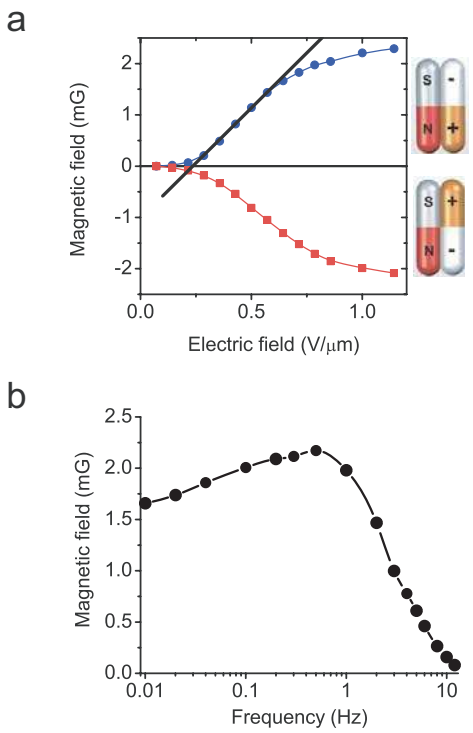

FIG. 5: (color online) (a) Measured magnetic field as a function of a 1 Hz sinusoidal electric field. The detected magnetizations are in phase (parallel: blue dots) and out of phase (antiparallel: red squares) with the applied electric fields. The parallel and antiparallel moments give rise to magnetizations of opposite sign for the same applied electric field. The straight line is a linear fit to the approximately linear region of the graph. (b) Indiced magnetic field as a function of the frequency of the applied electric field. At high frequency the rotational drag is larger than the applied resulting in incomplete rotation of the ME particles and therefore diminished induced magnetizations. For lower frequencies there is a slight reduction in magnetization as here the adhesion of the beads becomes stronger the longer the beads are in contact with the walls of the cavity. Note that magnetic fields due to currents and not due to the ME effect, become larger with increasing frequency, and are negligible in the present setup.

leakage currents cause a loss of charge and hence voltage before the magnetic field reverses sign, as is seen in Figure 4. The unmagnetized sheet exhibits no ME effect, whereas the parallel and anti-parallel particles give rise to a ME response that is of approximately equal magnitude and of opposite sign.

To understand the ME response in more detail, one needs to consider the dynamics of the ME beads. The orientation of the beads is to first approximation described by equating the torque due to the applied field with the rotational drag of the particles [5]. In addition, the particles experience adhesion forces when they come into contact with the walls of the cavity. However, each bead also possesses a net positive charge. When a large enough voltage is applied to the medium, then the charge permits the particles to be pulled away from the cavity wall so that they are free to rotate. If one considers a collection of identical particles, then, in the limit of static fields, one would expect the response of the sheet to be described by a step function: no magnetization for fields that are too small to overcome the adhesion force, and otherwise the full saturation magnetization. Both the off-set voltages as well as the saturation magnetization (corresponding to complete alignment of the beads) is seen in the experimental data shown in Figure 5a. The intermediate region of the graph is sigmoidal, which is partly explained by the variance of the bead properties and hence the distribution of adhesion potentials. If we only consider the region that exhibits approximately linear magnetoelectric coupling, and write

$$\vec{M} \approx \chi \vec{E} \quad \text{and} \quad \vec{P} \approx \chi \vec{B} \,, \tag{1}$$

where $\vec{M}$ is the bulk magnetization and $\vec{P}$ the polarization, with $\vec{E}$ and $\vec{B}$, respectively, the electric and magnetic fields, then we find from a linear fit to the data that χ=0.4 ps/m (=0.07 mV/(cm Oe) = 3×10^{-7} A/V). Surprisingly, the magnetoelectric coefficient of our isotropic ME medium is already not much smaller than coefficients found in ME crystals, such as chromium oxide, where χ_{zz}=4.1 ps/m at 270 K [1]. The magnetic moment of the ME beads, and hence the ME effect, can be significantly increased without compromising the functionality of the material.

We note that the medium exhibits dynamical hysteresis, i.e. the graph in Figure 5a is a function of frequency, as is seen in the measurements shown in Figure 5b.

Tellegen assumed that the particles with coupled permanent electric and magnetic moments should behave linearly, as this is advantageous for a network element [6]. It is important to realize that the ME particles need to

interact with each other or their surroundings as otherwise they could not be re-oriented by the field once they are all perfectly aligned. The nature of these interactions will therefore determine the particular functional form of the ME response. This will in general not be linear, as is for instance seen in Fig. 5a. One might, nevertheless, expect that the present system can be operated in its linear range by application of a dc bias and a small ac field of an appropriate frequency, as is for instance done in ordered ME composites that exhibit a nonlinear ME effect [21]. However, we found the statistical distribution of the bead release times from the cavity wall was too large to allow this possibility to be tested with the current system. Interestingly, the question of whether the magnetoelectric particles envisioned by Tellegen, can give rise to a linear ME effect is the subject of an ongoing theoretical debate [8, 22, 23]. Now, that we have shown that ME particles according to Tellegen's recipe can be used to make a ME medium, it will be a topic of future research to establish if this or a related system can be devised which permits the observation of a linear ME effect.

In summray, we have made particles with coupled permanent magnetic and electric moments and used these to fabricate a switcheable, room-temperature ME material that is isotropic in the absence of any field. It exhibits a ME response which results from the orientation of the constituent particles. The motion of the magnetoelectric particles itself is now an integral part of the material's response, and this may be exploited in applications. Should the particles be optically anisotropic, as in this particular case, then ME properties can be studied optically, which should prove particularly useful in the characterization of a whole host of potential new magnetoelectric particles, including colloidal and nano-sized particles. Complex electromagnetic, rheological, and dynamical effects are expected in this new class of magnetoelectrics. Finally, the combination of electric and magnetic moments in a single particle introduces a new handle in the manipulation of micro- and nanoparticles and is thus expected to be a generally useful property that should find application in other fields.

Acknowledgements: We thank Winfield Hill for help with the electronics, David Phillips for the loan of the fluxgate and the Rowland Institute for financial support.
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